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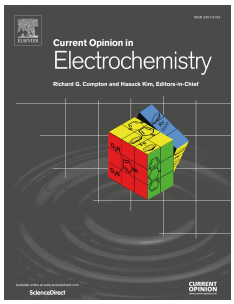

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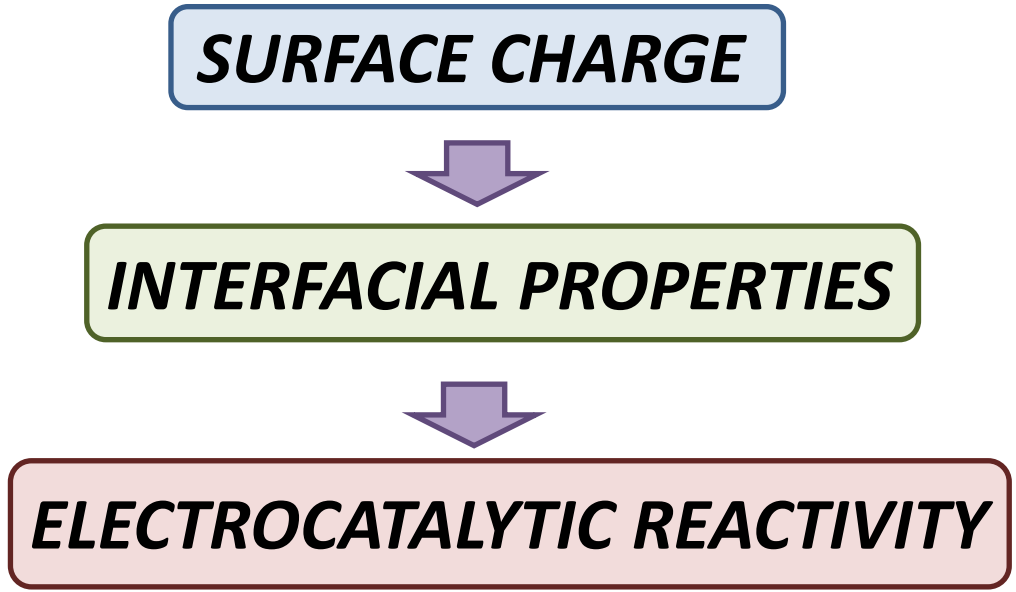
SURFACE CHARGE
INTERFACIAL PROPERTIES
ELECTROCATALYTIC REACTIVITY

Pt(hkl) surface charge and reactivity

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Summary

Interfacial charge has a decisive influence on the reactivity of the most common electrochemical reactions for practical applications. In this work, the concepts of surface charge and the different types of potential of zero charge (pzc) are revised on model electrodes. The different methodologies for the determination of the pzc are reviewed. After that, a thorough examination of the effect of surface charge on different electrochemical reactions of interest is carried out. The acid-base dissociation constants on the surface or the kinetics of relevant electrocatalytic reactions such as nitrate and peroxodisulfate reduction, formic acid oxidation, oxygen and hydrogen peroxide reduction or hydrogen evolution are affected by the interfacial charge. Therefore, it is crucial to understand the surface charge characteristics of the electrode materials in order to obtain the better electrocatalytic activity.

Keywords

surface charge

platinum

single crystals

electrocatalysis

interfacial properties

pzc

Introduction

The properties of the electrified interphase, which is formed between electrode and solution, govern the electrocatalytic reactions [1]. Among them, the interfacial charge is of paramount importance in the electrochemical reactivity, since the interactions of molecules and ions with the electrode surface are affected by the sign and magnitude of the charge separation in this narrow region [2-4]. The most used parameter for connecting the surface charge with the electrode potential is the potential of zero charge (pzc), which was first introduced by Frumkin in 1928 [5]. It can be defined as the potential at which there is no excess charge on the electrode surface [6]. For materials on which the formation of the electrochemical interface implies adsorption processes with charge transfer, i.e. Pt or Pd electrodes, two types of pzc should be considered: the potential of zero free charge (pzfc) and the potential of zero total charge (pztc) [6, 7]. The pzfc only considers the true electronic excess charge compensated by the ions in the electrolyte, while the pztc includes the charge involved in adsorption processes [2, 6, 7]. The pztc is usually the accessible magnitude by electrochemical experiments, and can be determined using a pure thermodynamic approach, while the pzfc should be estimated within a model [8].

CO displacement experiments have been commonly used to determine the pztc on Pt electrodes [2, 9-15]. The most used procedure consists in integrating the voltammetric currents to obtain the charge vs. potential plot by using the total charge measured in CO displacement experiments at a certain constant potential (usually 0.1 V vs. RHE) as the integration constant. The pztc is determined from this plot as the potential value for which the charge is zero [14]. The pzfc can be estimated from these measurements as the linear extrapolation of the charge from the double layer region into the hydrogen or OH regions (for acid and alkaline media, respectively) [2, 13]. This

value was previously called potential of zero extrapolated charge (pzec) and it is a good approximation for the pzfc in acidic solutions, but there exists more uncertainty for alkaline solutions [13].

Besides the non-thermodynamic assumptions from the pztc, the pzfc can also be estimated indirectly by laser-induced temperature jump (LITJ) experiments [16-22]. This methodology uses nanosecond laser pulses for increasing the temperature at the interface, and its response to this perturbation under coulostatic conditions gives information about the net orientation of water at the interface. The potential value at which no signal is recorded corresponds to the situation in which the water molecules are totally disordered, and therefore this potential is called potential of maximum entropy (pme) [16]. The pzfc can be approximated to the pme, since the situation of zero charge would lead to the total disorder of the water adlayer [16, 19]. This technique allowed to confirm the pzfc for Pt(111) at pH values ranging from 1 to 5 [19, 22, 23], and pointed out that there are local pzfc for steps and terraces on Pt stepped surfaces [19]. In addition, LITJ experiments demonstrated changes in the structure of ions at the Pt(111)/ionic liquid interfaces as a function of the electrode potential [20], and helped to explore the pme of the basal Au(hkl) planes in contact with a room temperature ionic liquid [21].

Frumkin et al. observed two different pzfc on Pt, one at low potentials and other near the region of oxide formation [7]. LITJ experiments also indicated the existence of these pzfc at ca. the same potentials [18]. Recent theoretical studies by Huang et al. revealed a non-monotonic behaviour for the surface charge in Pt arising from the formation of a submonolayer of oxygen adatoms at the surface [24-26], which supports experimental results [7, 18]. The existence of these three different charge regions can also have an impact towards electrocatalytic reactions.

Although the effect of surface charge is known since the pioneering works of Frumkin [27], the specific role in determining the reactivity has not been considered until recently. In this review, its effect on important electrochemical reactions from a fundamental and applied point of view is discussed.

Bulk pK_a vs. surface pK_a

The surface charge of electrode surfaces is the responsible for the composition of the electrochemical interphase being different from that of the bulk of the solution. In this sense, the acid-base equilibria is affected by the charge, because of the interaction of the species with the surface. Thus, several examples of different distribution of the species in the interphase can be found. The ratio of adsorbed oxalate and bioxalate anions from oxalic acid on Au electrodes at different pH values was studied by Fourier transform infrared reflection absorption spectroscopy (FT-IRRAS) and surface-enhanced infrared absorption spectroscopy in the ATR configuration (ATR-SEIRAS) experiments [28]. It was observed that the bands related to the bioxalate species disappear for pH = 3, and therefore the predominant species at this pH would be oxalate anions, unlike the behaviour of the bulk solution. In the light of these results the authors proposed that the pK_a for the equilibrium between bioxalate and oxalate anions is lower on the electrode surface that in the solution. Similar observations were made for malonic and succinic acids in gold electrodes [29], but the quantitative effect on the pK_a was different. It was proposed that the smaller change in the latter case was due to the longer distance to the metal surface of the carboxylate group to the electrode surface leading thus to a different effect of the metal surface charge on the electrostatic potential affecting this functional group [29]. Yaguchi et al. investigated the adsorption of the phosphate anions at different pH values on Au(111) by ATR-SEIRAS and DFT

calculations [30]. They also concluded that the pK_a for the equilibriums of the adsorbed anionic phosphate species is different from the corresponding value in the bulk of the solution (Figure 1A). Although the above-mentioned investigations were performed with gold electrodes which are not totally well defined surfaces, they are very good examples for understanding this topic. In our group, these phenomena were also studied in well-defined Pt surfaces. The adsorption of carbonate and bicarbonate on Pt(111) from CO_2 saturated solutions was examined, and the results pointed out that at pH = 1 both anions are adsorbed (Figure 1B), indicating that the acidity of adsorbed bicarbonate anion is much higher than that in solution [31, 32]. This behaviour was explained in terms of an inductive effect toward the acidity of the anions by the positive polarization of the electrode or a direct effect of the electrical field generated on the interface. In the case of Pd/Pt(111) electrode only the adsorption of bicarbonate is detected in the whole range of potentials. Since the Lewis acid character of this electrode is lower than the Pt(111) electrode, the change in the surface acid constant is not as high as for Pt(111) electrode [31]. The adsorption of oxalic acid and its derived species were also studied on Pt single crystal electrodes. It was observed that oxalate anions are adsorbed at the Pt(100) electrode surface while bioxalate anions are the adsorbed species at Pt(111) [33].

The charge in the electrode surfaces can also affect to the acid-base behaviour of water in the electrochemical surface. While some authors claim that surface water is acidic others propose the opposite [34-38]. In any case, the different acidity of water near the electrode surface can affect the electrocatalyitic activity of reactions in which water plays an important role, i.e. ORR.

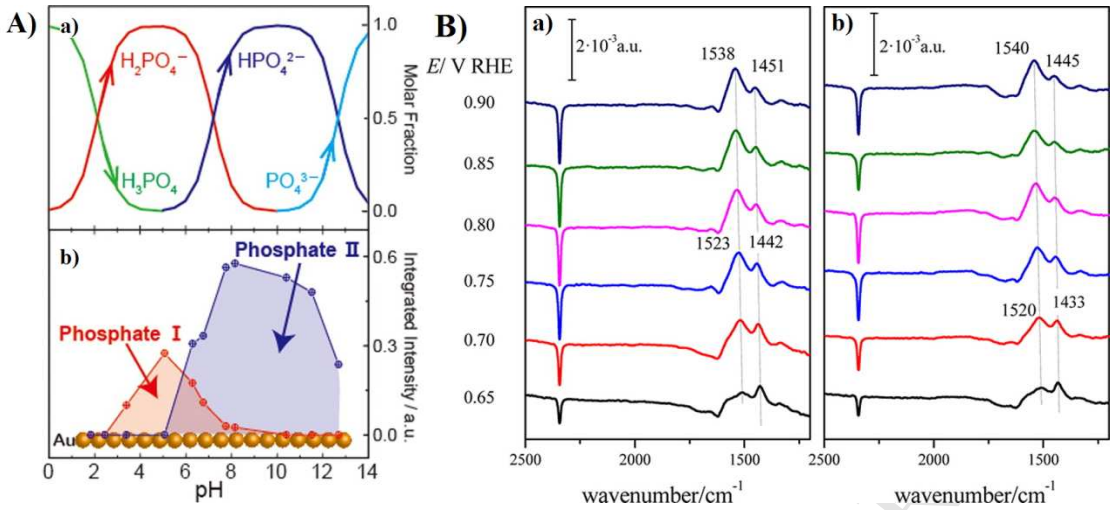

Figure 1: Molar fraction of the anionic phosphate species in the bulk solution at the different pH values (A, a). Intensities of the bands for Phosphate I ($H_2PO_4^-$) and Phosphate II (HPO_4^{2-}) on thin-film Au(111) at 1.0 V vs. RHE measured by ATR-SEIRAS (A, b). Adapted from Ref. [30]. FT-IRRAS spectra for Pt(111) in CO_2 saturated solutions at pH = 1.56 (B, a) and pH = 2.47 (B, b); the spectrum was collected at 0.1 V vs. RHE. Adapted from Ref. [32].

N_2O and peroxodisulfate (PDS) reduction reactions

N_2O reduction reaction has been traditionally used for the estimation of the pztc on platinum electrodes [39, 40]. This is because the maximum of the N_2O reduction coincides with the pztc of the surface, as observed for Pt single crystal electrodes [39]. Moreover, it was also observed that N_2O reduction is sensitive to the local pztc of terraces and steps on Pt stepped surfaces: the reduction maximum coincides with the pztc of the terrace and it decreases its intensity with the number of steps, while a local maximum appears near the pztc of the step (Figure 2A) [40]. Peroxodisulfate (PDS) anion reduction is also sensitive to the surface charge of the metal surface on Pt(111) at different pH values and also on Pt(100) and Pt(110) [41]. Remarkably, the potential value for the maximum of N_2O reduction coincides with the value in which PDS reduction current becomes zero (Figure 2B) [42]. These differences arise from the fact that N_2O is a neutral molecule interacting weakly with the surface, while PDS is an anionic species. The current drop in the current density of PDS reduction can be

identified with the point where the surface charge changes from positive to negative values [42]. As a result, PDS has been proposed as a probe molecule for the determination of the pzfc of Pt electrodes [3, 42]. The latest results with Pt stepped surfaces indicate that it can also be used to estimate the local charge properties of terraces and steps [3]. In addition, the use of PDS points out the existence of two pzfc values [7, 18, 24], since the onset of the reduction coincides with the pzfc near the oxide region and the potential value in which current density becomes zero again correspond to the pzc at low potentials [3, 26, 42]. A similar phenomena for this non-monotonic behaviour was observed recently on Au and Ag by Safonov et al. by impedance measurements in acetonitrile and aqueous solutions [43].

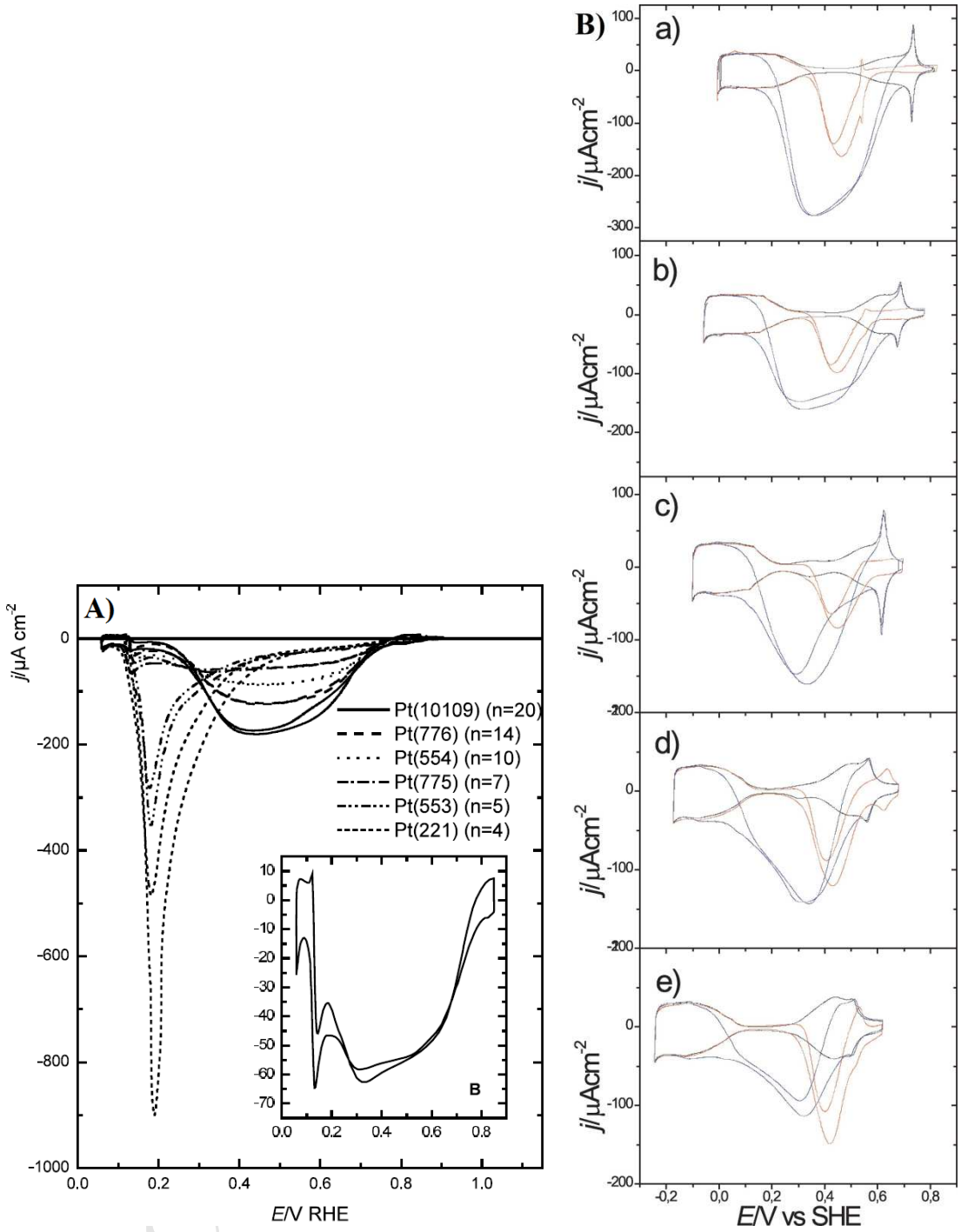

Figure 2: Cyclic voltammetry measurements for N_2O reduction on different Pt stepped surfaces in 0.1 M $HClO_4$ solution saturated with N_2O; scan rate: 10 mV s^{-1} (A). Adapted from Ref. [40]. Blank voltammograms (black), PDS (red) and N_2O (blue) reduction currents at pH = 1.1 (a), 2.1 (b), 3.0 (c), 4.1 (d) and 5.0 (e) in solutions prepared with NaF/$HClO_4$ mixtures; scan rate: 50 mV s^{-1} (B) Adapted from Ref. [42].

Formic acid oxidation reaction (FAOR)

The charge properties of the electrode surface can also affect the electrocatalysis of formic acid oxidation. This reaction is inhibited by the formation of CO intermediate [44]. On Pt(100), the formation of this poison is maximal at the pztc [45, 46], and therefore the highest inhibition rate takes place at potentials around this potential value. At the same time, the negative charge of the Pt(111) surface at pH values ranging between 5 and 10 promotes the interaction with the formate anion intermediate in the C-H down configuration, which is the active intermediate [47]. Other example of the influence of the surface charge on this reaction is the effect of the presence of adatoms or other molecules [48-50]. The adsorption of the adatom leads to a surface charge redistribution which modifies the electrode reactivity. When positive charge is located on the adatom, which happens for p-block metals less electronegative than platinum, the adsorption of formate intermediate in the C-H down configuration and the cleavage of this bond is favoured (Figure 3) [48, 49].

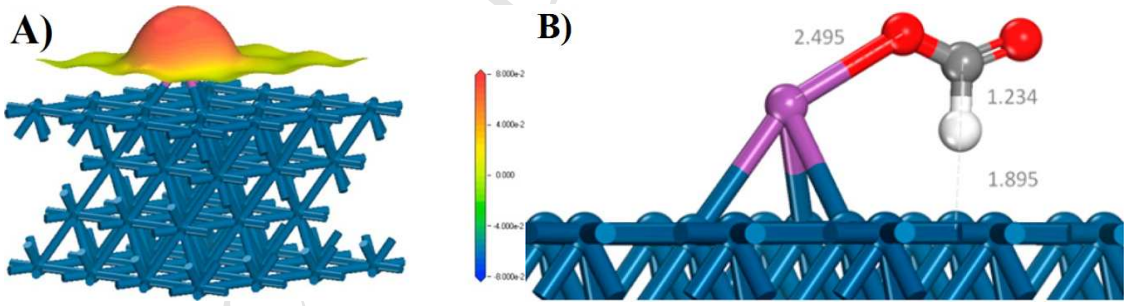

Figure 3: Electrostatic potential [Ha/e] mapped on electron isodensity surface for a density value ρ = 0.01 e/Å^3 for a Bi adatom adsorbed on the Pt(111) surface (A). Formate adsorbed in the C-H down configuration on the Bi-Pt(111) surface (B). Adapted from Ref. [48].

Oxygen Reduction Reaction (ORR)

ORR was studied on the Pt basal planes and different stepped surfaces at pH values from 1 to 6 and from 11 to 13 (Figure 4A) [51]. These are the accessible pH values without the use of buffering species that specifically adsorb on Pt [13, 22, 23,

51]. By this way it is possible to study the effect of the surface charge in the absence of any interference of other adsorbed species. Results pointed out that the kinetic current densities at 0.85 V vs. RHE follows a volcano trend for Pt(111) with its maximum centred at ca. pH = 9 (Figure 4B). It was proposed that this behaviour is because at this pH value the pzfc is close to the onset potential for the ORR [51]. Therefore, at pH = 9 the best conditions in terms of surface charge for this reaction occur. In addition, the structure of interfacial water could be also considered, since the pzfc is very near to the pme, at which value the water molecules near the electrode surface are totally disordered. This disordered layer would facilitate the reaction [51]. For Pt(100) and Pt(110) the situation is different, and they show a slightly monotonic decrease of the electrocatalytic activity as the pH increases (Figure 4B). This is because for these surface the ORR always takes place with a constant coverage of OH species, while the adsorbed OH on Pt(111) in the region of interest (0.3 to 0.7 V vs. RHE) is more labile [51]. For the stepped surfaces an intermediate situation is observed (Figure 4B), since the electrocatalytic activity depends on the terrace length.

It can be also observed in Fig. 4A that the limiting current density for decreases progressively from pH = 3 as the solution pH is increased. This behaviour is not observed for the hydrogen peroxide reduction [51]. This suggests the existence of a bifurcation point in the ORR mechanism before the formation of H_2O_2, and it was proposed that it could be the formation of soluble $OOH^{\bullet}$ [52-54], an intermediate detected at the surface [55]. The decrease in the limiting current density at pH values higher than 3 could be due to the acid-base equilibrium of $OOH^{\bullet}$, whose pK_a is 4.8 [54] but it could be modified by the surface charge, or to the different acid-base properties of interfacial water.

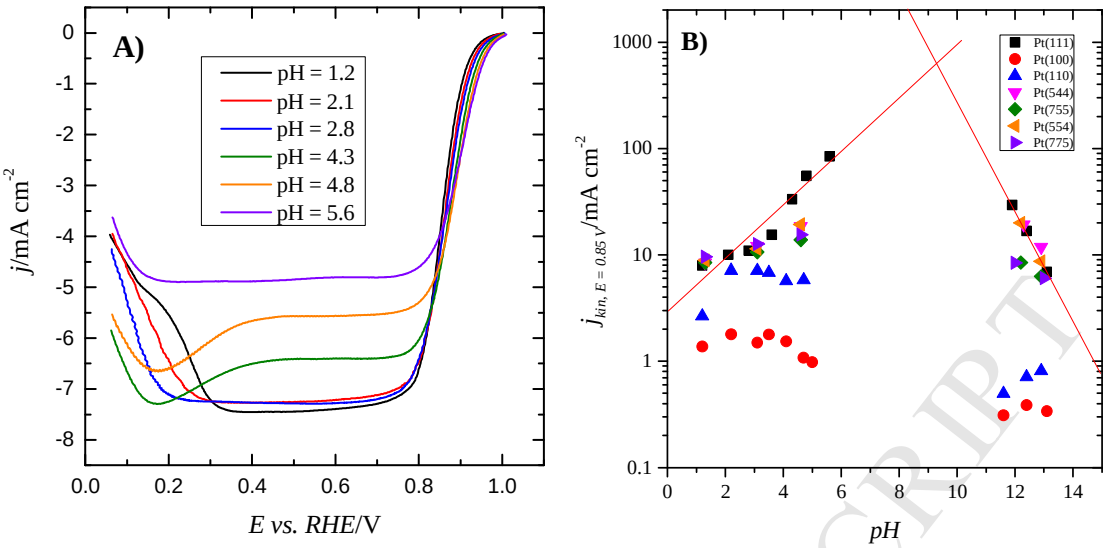

Figure 4: Polarization curves for the ORR on Pt(111) in solutions with different pH values prepared with $NaF/HClO_4$ mixtures and saturated with O_2; scan rate: 50 mV s^{-1}; rotation rate: 2500 rpm (A). Kinetic current densities at 0.85 V vs. RHE for the indicated well-oriented Pt surfaces at different pH values (B). Adapted from Ref. [51].

Hydrogen peroxide reduction reaction (HPRR)

HPRR was also studied on Pt(111) from acidic to neutral pH values [56]. Results showed that the current inhibition that takes place at low potentials on the Pt(111) electrode starts at the same potential in the SHE scale (ca. 0.36 V vs. RHE) for all the pH values (Figure 5A). This inhibition was previously attributed to hydrogen adsorption, which would hinder the scission of the O-O bond by occupying the μ-peroxo adsorption sites [57, 58]. However, the pzfc and the interfacial water structure are related to this behaviour, since 0.36 V vs. RHE is very close to the pme for Pt(111) [19, 23]. Experiments for pH = 2 in the absence and in presence of K^+ indicate that the presence of cations has a different effect towards the ORR and the HPRR (Figure 5B) [59]. This reflects that the different interaction of O_2 and H_2O_2 molecules with the electrical field and the cations leads them to different reaction pathways. Experiments for both reactions in the presence of Br^- also suggest that during the ORR other intermediate different to H_2O_2 is likely to be formed [59]. The adsorption of Br^- on

Pt(111) at the different pH values always take place at the same potential in the SHE scale, since the process does not involve the transfer of protons and therefore only depends on the surface charge of the electrode [14].

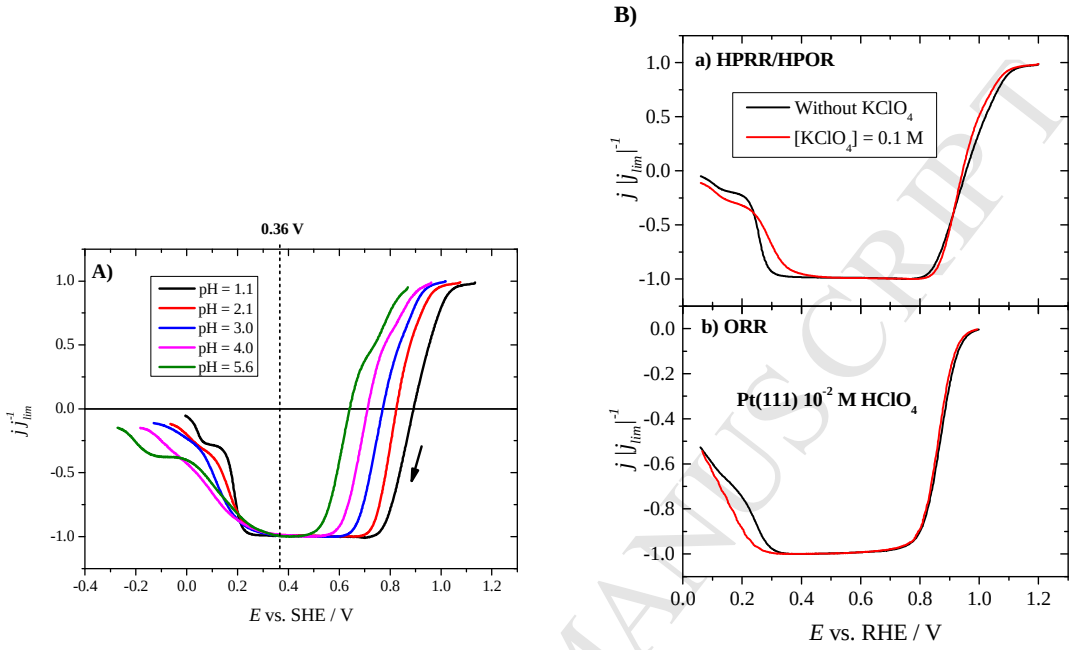

Figure 5: Polarization curves for the HPRR/HPOR on Pt(111) in solutions with different pH values prepared with $NaF/HClO_4$ mixtures and 1.7 mM H_2O_2; scan rate: 50 mV s^{-1}, rotation rate: 2500 rpm. The dotted line marks the potential in which the inhibition starts for all the pH values (A). Adapted from Ref. [56]. Comparison of the HPRR/HPOR (a) and the ORR (b) in pH = 2 in the absence and in presence of 0.1 M K^+; scan rate: 50 mV s^{-1}, rotation rate: 2500 rpm (B). Adapted from Ref. [59].

Hydrogen evolution reaction (HER)

A recent study pointed out that not only the HER but also the kinetics for the hydrogen adsorption are slower in alkaline than in acidic media [60]. Therefore, the pH-dependent shift for the hydrogen binding energy, which has been traditionally used as a descriptor for the HER kinetics [61-64], is not enough to explain the differences between both media. Measurements with Pt(111) modified with Ni showed that when the pme for the electrode surface is near the onset potential for the HER and the hydrogen adsorption potential, the electrocatalytic activity is maximal [60]. This explanation is based on the less rigid or more disordered water adlayer at the pme, close

to the pzfc and therefore implying a weak interaction with the interfacial electric field. This disordered interfacial adlayer could reorganize easily favouring the kinetics of the reaction. Studies with different Ni coverages support this hypothesis, since different pme are systematically observed [65].

The electrochemical interface between Pt(hkl) and non-aqueous solvents

Although this work mainly focuses on works performed with aqueous solutions, the use of non-aqueous solutions such as ionic liquids is important in many fields, e.g. electrocatalysis, electodeposition or batteries and supercapacitors. Despite the numerous contributions using this type of electrolytes, the number of works about the electrochemical interphase between well-defined surfaces and non-aqueous solutions is still scarce. The main challenge of non-aqueous solutions is that they usually contain a higher amount of impurities than aqueous solutions. Since Pt surfaces are very catalytic and they have a strong tendency to adsorb the different components of the solution, it is difficult to systematically study the relation between surface charge and reactivity without the interference of impurities. The work by Gnahm and Kolb [66] supposed a great advance in the purification of ionic liquids, and allowed studying the hydrogen oxidation at the Pt(hkl) and ionic liquid interfaces [67, 68]. In addition, due to the ionic nature of the ionic liquids, the analysis of capacitance data using the Gouy-Chapman-Stern model is not possible, and besides the coulombic interactions, the hydrogen bonding between anions and cations should also be considered. In this sense, the LITJ has been demonstrated to be a valuable technique for the study of the interface structure in these cases [20]. All the above-mentioned contributions opened the door to future works which could investigate the influence of the surface charge on the electrocatalytic activity of reactions of interest.

Conclusions

The effect of the surface charge on different electrochemical reactions has been summarized. In addition to the CO displacement and LITJ experiments, the sensitivity to the surface charge of the reactions presented here reveals that the reactivity is significantly altered. Reduction of N_2O and PDS allows probing the local pzc on platinum stepped surfaces. On the other hand, several examples (FAOR, ORR, HER and HPRR) also demonstrate how the charge alters the reaction rates.

All the results exposed here clearly indicate that surface charge plays an important local role on electrocatalysis. These factors have to be taken into account to fully understand the reaction mechanisms, so that more efficient electrode materials could be envisaged from a rational design perspective and help to stablish the specific conditions for the best performance of the electrocatalysts.

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Conflicts of Interest

The authors have no competing interests to declare.

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[2] •• The pztc and pzfc are investigated for Pt(111) in a wide range of pH values by using the CO displacement method.

[3] • In this review the concept of surface charge is revised and the different experimental and theoretical strategies for its determination are summarized.

[13] •• The variation of the pztc and pzfc is studied in the pH range from 3 to 5 by CO displacement using NaF/$HClO_4$ mixtures in order to avoid anions specific adsorption.

[19] • Local pme for terraces and steps are examined for Pt stepped surfaces at pH 1 and 3 by using the LITJ technique.

[22] •• The pme for Pt(111) in the pH neutral region from 3 to 6 is determined by the LITJ technique in the absence of anion specific adsorption.

[24] • A new structural model for the electrified interface is presented taking in to account the formation of surface oxide and the orientation of interfacial water, and its analytical solution reveals a non-monotonical charging behaviour.

[30] •• ATR-SEIRAS measurements and DFT calculations revealed that the pK_a for adsorbed phosphate species in Au is much lower that for the same species in the bulk solution.

[32] • FT-IRRAS results show that at pH = 1 there is carbonate and bicarbonate adsorption on Pt(111), while the bulk concentration of these species is negligible.

[40] • The pztc for Pt stepped surfaces are determined by CO displacement and using N_2O as a local molecular probe for the surface charge.

[42] •• PDS reduction is studied in a wide pH range. It is observed that the complete inhibition for the reaction occurs at potentials lower than the pzfc.

[49] •• The effect of the presence of adatoms on Pt(111) towards the formic acid oxidation reaction is studied by means of cyclic voltammetry experiments and DFT calculations.

[51] •• ORR is studied from acid to neutral pH values and in alkaline media in the absence of specific anion adsorption on different Pt single crystal electrodes.

[55] •• $OOH^{\bullet}$ intermediate is detected spectroscopically in Pt(111) by using the EC-SHINERS technique

[56] •• HPRR and HPOR are studied from pH 1.1 to 5.4 on Pt(111). Results show that the inhibition at low potential is related to the Pt surface charge.

[59] • New aspects for the ORR mechanisms are pointed out by cyclic voltammetry measurements made in presence of bromide or solutions with different ionic strength

[60] •• The effect of water reorganization towards the HER as a result of changes in the pzfc is investigated by modification of Pt(111) with Ni.

[65] • Different degrees of Ni coverage are used to study the effect of the pzfc towards the HER on Pt(111) modified electrodes.

Conflict of Interest : Uploaded by JM